Analyte:	Ethyl silicate	Method No.:	S264
Matrix:	Air	Range:	377-1620 mg/cu m
OSHA Standard:	100 ppm (850 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on XAD-2 resin, desorption with carbon disulfide, GC	Validation Date:	2/27/76

1. Principle of the Method

A known volume of air is drawn through a tube containing XAD-2 resin to adsorb the ethyl silicate present.

1.2 The XAD-2 resin in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 377-1620 mg/cu m at an atmospheric temperature and pressure of 21°C and 771 mm Hg, using a 9-liter sample. Under the conditions of sample size (9 liters) the probable useful range of this method is 85-1700 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 15-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used. When higher concentrations of ethyl silicate are expected, a smaller sample volume should be collected.

The upper limit of the range of the method is dependent on the adsorptive capacity of the XAD-2 resin tube. This capacity varies with the concentrations of analyte and other substances in the air. Breakthrough studies indicated that the first section of the XAD-2 resin tube was found to hold 24 mg of analyte when a test atmosphere containing 1640 mg/cu m of analyte in air was sampled at 0.80 liter per minute for 18 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent.

The collection efficiency of ethyl silicate on the XAD-2 resin tube may be dependent on sample flow rate. A separate study gave a collection efficiency of 98% for 9-liter samples collected at 0.067 liter per minute for concentration levels at 2 times the OSHA standard.

The resin tube consists of two sections of XAD-2 resin separated by a section of silylated glass wool. (See Section 6.2) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

The adsorptive capacity of XAD-2 resin is not severely affected by water vapor. Breakthrough volume will not be substantially affected by high relative humidity. Note, however, that although ethyl silicate is not soluble in water, it is slowly decomposed by water (Merck Index).

When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 377-1620 mg/cu m was 0.056. This value corresponds to a 48 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 7.1% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the resin tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.2)

Resin tubes: glass tube with both ends flame-sealed, 7 cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin, prepared as described in Section 7.7. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the outlet end of the tube and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

Gas chromatograph equipped with a flame ionization detector.

Column (10-ft x 1/8 in. stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.

An electronic integrator or some other suitable method for measuring peak areas.

Sample containers, 5-ml, with glass stoppers or Teflon-lined caps.

Microliter syringes: 10-microliter, and other convenient sizes for making standards

6.8 Pipets: 2.0 ml, delivery type.

Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

6.10 Glass rods, 3 mm, or cylindrical wooden medical applicators.

7. Reagents

Chromatographic quality carbon disulfide

Ethyl silicate, reagent grade

Nonane, or other suitable internal standard

Purified nitrogen

Prepurified hydrogen

Filtered compressed air

Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a standard Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hr) extractions are then performed successively with water, methyl alcohol, diethyl ether and, finally, n-pentane. Distilled-in-glass solvents are used in all cases. Resin has been prepared successfully in this manner using charges of about 700 g of resin and 1.5 liters of each solvent. The resin is dried by maintaining it under vacuum (1-10 torr) and mild heat for about 24 hours.

8. Procedure

Cleaning of equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

Calibration of Personal Pumps. Each personal pump must be calibrated with a representative XAD-2 resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of XAD-2 resin is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The XAD-2 resin tube should be placed in a vertical direction during sampling to minimize channeling through the resin.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the coated XAD-2 resin tube.

8.3.5 A maximum sample size of 9 liters is recommended. Sample at a rate of 0.05 liter per minute only. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The XAD-2 resin tubes should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube for every 10 samples should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped XAD-2 resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of samples

1. In preparation for analysis, each sample tube is scored with a file in front of the backup and the front section and broken open at both ends to give a wider tube opening for easier transfer of the resin bed.

2. Remove the glass wool plug next to the backup section (exit end) and discard. Transfer the resin from the backup section into a 5-ml vial.

3. Then remove the glass wool plug at the front end of the 100 mg section and transfer to a separate 5-ml vial. Carefully transfer the resin into the same

5-ml vial. If the resin particles tend to hang on to the inner walls of the glass tube instead of flowing freely, use the remaining glass wool plug to push out the rest of the resin particles. A short piece of 3-mm glass rod or a wooden medical applicator can be used for this purpose.

4. In the event that difficulties are encountered in the transfer operation due to electrostatic charges which make the resin particles cling to the glass walls, it is suggested that the tubes be flushed with a gentle stream of air or nitrogen presaturated with water for 5-10 seconds.

8.4.2 Desorption of Samples. Prior to analysis, 2.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 ml of carbon disulfide containing a known amount of the chosen internal standard. If an automatic sample injector is used, transfer at least a 1-ml aliquot of the desorbed sample solution to the automatic sample injector vial.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 100°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket

of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of XAD-2 resin to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of XAD-2 resin is used.

8.5.2 Procedure for determining desorption efficiency. An amount of the XAD-2 resin equivalent to that present in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame-sealed at one end. This resin must be from the same batch as that used in obtaining the samples and can be obtained from unused XAD-2 resin tubes. The open end is capped with Parafilm. A known amount of ethyl silicate is injected directly into the resin with a microliter syringe, and the tube is capped with more Parafilm. Alternatively, a 5-ml vial capped with a Teflon-faced septum may be used in place of the glass tube.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 9-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the XAD-2 resin. These tubes are referred to as the samples. A parallel blank

tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 2.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the resin. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 2.0 ml of carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the ethyl silicate is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 2.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per 2.0 ml is plotted versus the ratio of the area of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID responses.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because

the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

Read the desorption efficiency from the curve (see Section 8.5.2 for the amount found in the front section). Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

At the recommended sampling rate of 0.05 liter per minute and a sample volume of 9.0 liters, no correction for collection efficiency is necessary. The collection efficiency was determined to be at least 98% under these conditions.

The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.7 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.